RECONSTRUCTION OF KNOWLEDGE OF THE ENVIRONMENT IN LATE ANTIQUITY IN THE AREA OF GORNO NOVO SELO VILLAGE

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Abstract: *The work aims to reconstruct the knowledge of the environment in the area of Gorno Novo Selo village during Late Antiquity by methods of archaeological chemistry. Such a study provides information on used raw materials and technologies applied in the past. The investigation of ancient mortar includes determining the phase composition, hydraulicity, and binder-aggregate ratio. Using X-ray fluorescence, chemical, and Powder X-ray diffraction analysis, Late Antique mortars from Bulgarian archaeological sites and associated geological resources were investigated. The obtained results confirm good knowledge of the environment in the residence territory during Late Antiquity and are of fundamental and practical use, helping a future archaeological interpretation.*

РЕКОНСТРУКЦИЯ НА ЗНАНИЯ ЗА ОКОЛНАТА СРЕДА ПРЕЗ КЪСНАТА АНТИЧНОСТ В РАЙОНА НА ГОРНО НОВО СЕЛО

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Ключови думи: *Реконструкция на знанията за околната среда, хоросан от Късна античност*

Резюме: *Целта на настоящата работа е да се направи реконструкция на знания за околната среда в района на Горно ново село през Късната античност чрез използването на методи на археологическата химия. Получените резултати ще предоставят информация за използваните суровини и технологии. Изследването на древен хоросан включва определяне на фазовия състав, хидравличността и съотношението „свързващо вещество-агрегат". Изследвани са късноантични проби от хоросан от български археологически обекти и проби от геоложки ресурси от района чрез химичен, рентгено-флуоресцентен анализ (XRF) и прахова рентгенова дифракция (PXRD). Получените резултати имат фундаментална стойност (потвърждават добро познаване на околната среда на обитаваната територия през Късната античност) и приложен характер (подпомагат интерпретацията на археологическите находки и обекти).*

Introduction

The methods used in modern archeology generally can be classified into two main groups – non-destructive (for the discovery, delineation, and mapping of archaeological sites) and destructive (for the study of artifacts). The first group includes field excavations [1] and geophysical methods such as ground-penetrating radar system (GPRS), geomagnetic and radiometric measurements, and remote sensing methods like drone and satellite photos survey, etc. [2]. The second includes methods

of archaeological chemistry such as chemical and X-ray fluorescence analysis, powder X-ray diffraction measurements, thermal analysis, etc. [3].

Archaeological artifacts, such as pottery and mortar, can be studied by archaeology chemistry methods [4, 5]. The study of ancient mortar includes determining the phase composition, hydraulicity, binder-aggregate ratio (B/A), and the potential source of raw materials used [3, 5, 6]. Mortar is a composite material prepared from a binder and aggregate. Slaked lime (portlandite, $Ca(OH)_2$), obtained by calcination of carbonate rocks (limestones, marls), was used as the raw material of the mortar binder. Over time the portlandite is replaced by calcite, i. e. the mortar hardens. In some mortars, in addition to calcite, hydraulic phases such as calcium hydro-silicates, mono-carboaluminates, etc., were found in the binder, imparting hydraulic properties to the mortar [6–8]. The formation of hydraulic phases can be by adding to the fresh mortar mixture the pozzolanic additives (volcanic ash, ceramic fragments, etc.) or clay rocks, which are high in Al and Si [7–9]. The binder is usually of silicate and aluminosilicate composition, most often of crushed silicate rocks or river sand, with the mineral composition of quartz, feldspar, and mica. The binder is an inert phase in the mortar, which creates the mortar's characteristic porous structure, preventing the formation of mold [6]. Clarifying the recipe for mortar preparation is necessary to determine the B/A ratio and the potential raw material for its production. Additionally, studying the phase composition of artifacts and comparing those with geological resources in the residence territory, provide information on raw materials and technologies used in the past.

This paper aims to make reconstruction of knowledge of the environment in the area of Gorno Novo Selo village during the Late Antiquity by examining mortar and local geological resource samples using X-ray fluorescence, chemical, and powder X-ray diffraction analysis. Such investigation also contributes to the conservation and reconstruction of archaeological sites.

Materials

Three mortar samples collected from two Late Antiquity archeological sites were studied. Both sites' location was in the region of Gorno Novo Selo village (Bulgaria). The selected area is of great importance for the central part of Sarnena Sredna Gora mountain, as the archaeological sites located there formed a settlement complex, defined as the regional management, economic and religious center [10]. The examined samples were: (i) a mortar sample № 1 from the site № 14 – Gorno Novo Selo, Sveti Nikola area. The site was defined as a fortified settlement with preserved fortress and church stone walls (Fig. 1), and ii) mortar samples № 17 and № 18 from site № 16 Gorno Novo Selo, church Extra Muros 2. The site was with preserved stone walls of church and building (Fig. 2). Samples № 1 and № 17 were collected from the church stone walls, and sample № 18 – was from the church floor made of bricks. At both archaeological sites, the stone walls were of gneisses, and tiles, bricks, also pottery were found.

Fig. 1. Archaeological site № 14

Fig. 2. Archaeological site № 16

To trace the raw materials used for mortar production, the rocks that outcrop on the earth's surface at the archaeological sites and close to them were investigated. Gneisses were found at the location of the two archeological sites, and limestones and marls to the south of the sites. Seven samples of these rocks were investigated: i) three samples of limestone – № 24.1, № 31.1, and № 31.3; ii) two samples of marls – № 32 and № 67, and iii) samples № 24.2 of fresh gneiss and № 4 of weathered gneiss.

Methods

X-ray fluorescence (XRF) analysis: The XRF analysis was performed by energy dispersive Micro-XRF Spectrometer M1 MISTRAL, Bruker (Rh-tube, Peltier cooling, 30 mm², Si-drift detector (SDD), MnKα resolution <150 eV, collimator 0.1 mm to 1.5 mm). The samples were prepared as pressed pellets with H_3BO_3 binder (1 g sample + 0.5 g H_3BO_3).

Chemical analysis: Moisture content determination: an equal amount of the mortar was dried at the temperature of T = 110°C. The dry mass of the samples was determined using an analytical balance. CO_2 amount determination: The powdered dried mortar samples were heated at T = 930°C in a porcelain crucible. The sample's CO_2 losses were determined using an analytical balance. Determination of binder aggregate ratio (B/A): the samples were solved with 1N HCl for 20 min. After the acid treatment, the obtained solutions were filtered, and the sediments were dried at T = 110°C and weighed [11, 12].

Powder X-ray diffraction (PXRD) analysis: The powder X-ray diffraction (PXRD) measurements were made by Empyrean, "Panalytical", CuKα radiation (λ = 0.15418 nm) (operating at 40 kV, 30 mA) from 5 to 90° 2θ with a step of 0.013 2θ, 30 s/step.

Microscopic observations: Levenhuk 3ST, 20-40x optical zoom.

Results and discussion

Table 1 shows the results of the XRF analysis of investigated rocks and mortars.

Table 1. Results of XRF analysis

Sample		wt%									
Type	**Number**	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**K_2O**	**CaO**	**Fe**	**Ti**	**Mn**	**S**
Limestone	№ 24.1	<LOD	0.60	1.60	0.15	<LOD	55.18	0.28	3.86	0.01	0.24
	№ 31.1	6.03	1.70	17.71	0.41	0.58	46.45	1.18	0.14	0.04	0.26
	№ 31.3	7.22	1.08	22.40	0.14	0.14	44.78	1.04	0.17	0.17	0.24
Marl	№ 32	<LOD	3.63	16.24	0.15	1.55	49.36	3.18	0.33	0.05	0.27
	№ 67	<LOD	3.70	22.44	0.10	1.42	43.24	3.60	0.32	0.08	0.11
Gneiss	№ 4	<LOD	14.33	67.29	<LOD	2.48	0.98	3.26	0.55	0.55	0.11
	№ 24.2	<LOD	14.19	64.19	0.44	3.37	0.57	0.55	0.04	0.03	0.43
Mortar	№ 1	2.56	7.39	50.21	0.32	1.73	17.00	1.20	0.11	0.04	0.02
	№ 17	2.74	8.34	50.64	0.18	1.65	10.24	1.20	0.11	0.03	0.03
	№ 18	4.23	8.44	44.77	0.11	1.64	17.21	1.21	0.12	<LOD	<LOD

LOD – limits of detection

The chemical composition of the rocks is as follows:

- Limestones: mainly by CaO with varying contents from 44.78% to 55.18%. The MgO – from values under limits of detection (LOD) up to 7.22%, which supposes that the main carbonate mineral in the limestones is calcite ($CaCO_3$). The SiO_2 was in concentrations from 1.60% to 22.40%, the Al_2O_3 - from 0.6% to 1.08%, which implies variable content of silicates in limestones. The low concentration of Al_2O_3 suggests that the aluminosilicates (clay minerals) were not present [13]. In this regard, the Si and Al variable content probably were of a sandy fraction - from a minimum amount (sample № 24.1) to a relatively high content in samples № 31.1 and № 31.3.
- Marls: mainly by CaO and SiO_2. The concentration of Al_2O_3 was higher than that of limestones which suggests the presence of aluminosilicate phases.
- Gneisses - metamorphic rocks, composed mainly of silicate and aluminosilicate minerals, which determines the results of chemical analyzes: mainly SiO_2 (34% - 37%) and Al_2O_3 (~ 14%), and a small amount of K_2O (2.48%) – 3.37%).

The mortar samples was composed mainly by CaO – from 10.24% up to 17.21%, SiO_2 – from 44.77% to 50,64%, and Al_2O_3 – from 7.39% to 8,44%. The MgO was measured from 2.56 up to 4.23%. K_2O, P, and Ti were measured in approximately equal quantities in all samples. The high content of Ca, the low content of Mn, and the low content of S suggest that the binder in the mortars was composed mainly of $CaCO_3$ (calcite). The low concentration of Fe, Ti, and Mn also suggests that these elements do not form their separate phases. The high content of Si and Al suggests that the mortar aggregate was composed mainly of silicate and aluminosilicate phases.

Figures 3, 4, and 5 show the results of rock PXRD analysis.

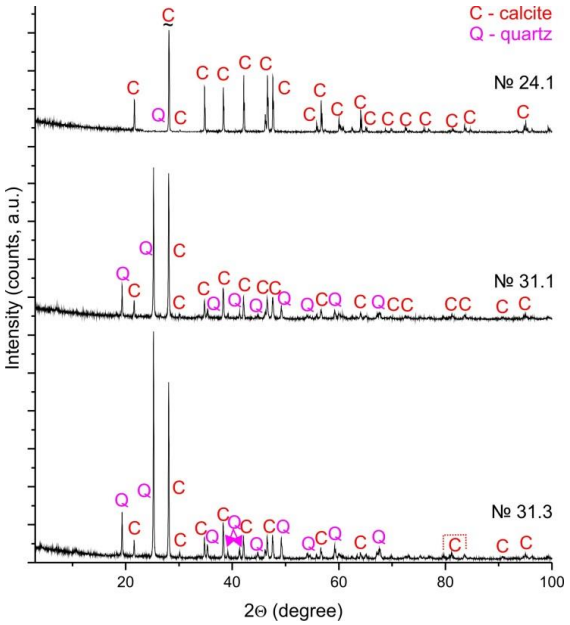

Fig. 3. PXRD patterns of limestones

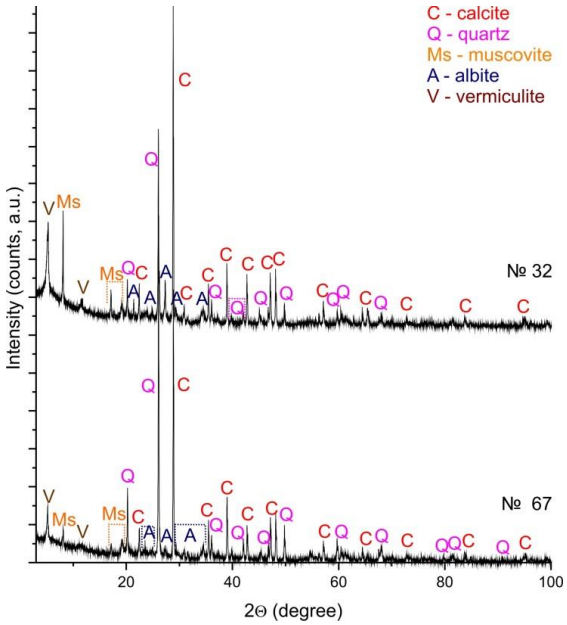

Fig. 4. PXRD patterns of marls

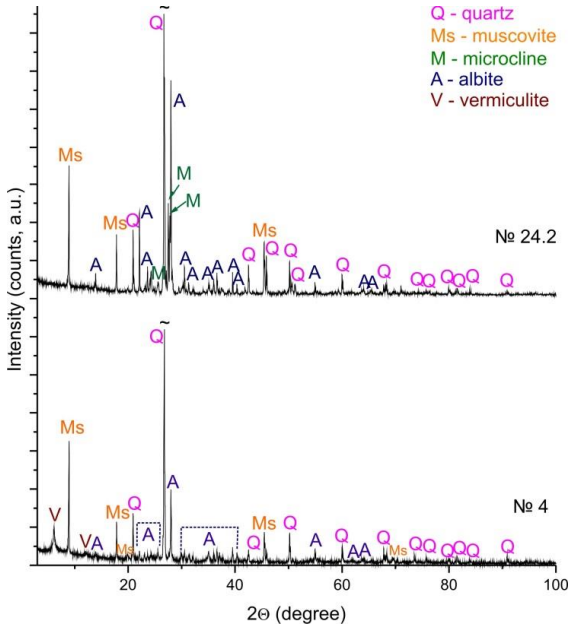

Fig. 5. PXRD patterns of gneisses

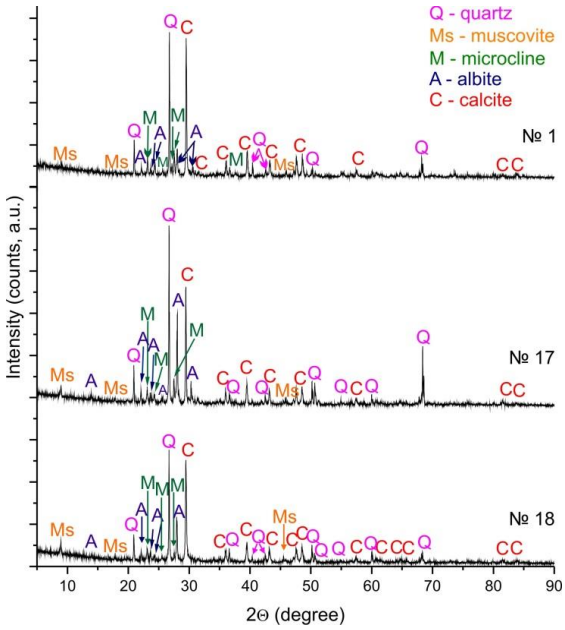

Fig. 6. PXRD patterns of mortars

All studied limestone samples (Fig. 3) were composed of calcite ($CaCO_3$ - PDF#06-6528 [14]) and quartz (SiO_2 - PDF#06-1757 [14]). The marls (Fig. 4) – of calcite, quartz, muscovite ($KAl_2(AlSi_3O_{10})(OH)_2$ [15]), albite ($Na(AlSi_3O_8)$ - PDF#89-6426 [14]), and vermiculite ($Mg_{0.7}(Mg,Fe,Al)_6(Si,Al)_8O_{20}(OH)_4.8H_2O$ [16]), a mineral of smectite group. The gneisses (Fig. 5) - of quartz, muscovite, microcline ($K(AlSi_3O_8)$ - PDF#19-0926 [14]), and albite. Vermiculite was also found only in sample № 4 - weathered gneiss, formed by alteration of micas [17].

Figure 6 shows the results of the mortar's PXRD analysis. All the studied samples were composed of calcite, quartz, muscovite, albite, and microcline. Vermiculite has not been identified as well as calcium-magnesium carbonate, and calcium sulfate phases.

According to PRXD analysis, the mortar samples were the same phase composition. The binder was composed only of calcite. The aggregate of mortars was composed of silicate and alumosilicate phases. The B/A ratio results (Table 2) show the main mortar phases are those of aggregate, while calcite is in the subordinate quantity. The portlandite ($Ca(OH)_2$) amount used for mortar preparation was also calculated – from 13.49 to 22.67%.

Table 2. $CaCO_3$, $Ca(OH)_2$, and binder/aggregate (B/A) ration in mortar samples

Sample	$CaCO_3$ (wt%)	$Ca(OH)_2$ (wt%)	aggregate (%)	B/A ratio
№ 1	30.26	22.39	69.74	0.43 (1:2)
№ 17	18.23	13.49	81.77	0.22 (1:4)
№ 18	30.63	22.67	69.34	0.44 (1:2)

The PXRD results of the mortar study show the absence of hydraulic phases, as the production of hydraulic mortar was known during this archaeological epoch [9, 18], and local raw materials (marls) and pozzolans (ceramic fragments) were available. When preparing the binder with marls, during marl's calcination the vermiculite would be decomposed with a separation of free and chemically active Al and Si ions [17]. These ions would formate the hydraulic phases during mortar hardeners. That shows the raw material for binder preparation was limestone. The absence of calcium aluminate hydraulic phases prevented the ettringite and thaumasite formation, thus delaying the mortar destruction over time [19]. The absence of gypsum ($CaSO_4.nH_2O$) in the mortar binder shows: (i) no use of imported raw material (at the area of the archaeological site were no known gypsum deposits); (ii) environmental conditions did not cause the gypsum formation (in archaeological mortars has been proved the sulfation processes were caused by acid rain [20]); and (iii) the sulfur content in rocks was insufficient (Table 1) and was not enough for gypsum deposition. All the results define investigated mortars as lime mortars without hydraulic properties. Their use for church walls and floor binding was suitable, as this type of mortar is an excellent permeable binder, keeping dry, i. e. protecting against mold.

The PXRD results prove that for mortar aggregate was used gneisses whose mineral composition correspond to that of the mortars. The vermiculite absence shows that the used gneisses were unweathered.

The mortar's aggregate (quartz) granulometry was inspected using microscopic observations. Results obtained show altered granulometric compositions: in sample № 18, the quartz was approximately one-dimensional, in samples № 1 and № 17 – with variable sizes from 1 – 2 mm approximately up to 15 mm. In quicklime production, raw limestones were placed crushed in the kilns, the milling was made after the calcination [21]. This approach allowed the limestone solid-phase impurities to pass into the mortar. That results determined sandy limestone (samples № 31.1 and № 31.3) as the most likely raw material.

Apart from the difference in aggregate granulometric compositions, the samples also show different B/A ratios (Table 2). Such variation can be explained by: (i) different recipes, depending on the mortar application; (ii) raw limestone with different amounts of sandy fraction, which violated the original recipe due to the inability to control the amount of $Ca(OH)_2$ used in the mortar; (iii) lacking a specific recipe for the mortar preparation. The samples № 1 and № 17 were collected by the church walls and are of different B/A ratios – 1:2 and 1:4, respectively. The sample № 18 – by the church floor with the B/A ratio is the same as sample № 1. The measured difference in the B/A ratio for samples № 1 and № 17 was quite big and cannot be achieved only by different amounts of sandy fraction in limestones. That confirms no connection between the B/A ratio and the purpose of the mortar used. The preparation of mortar with a high B/A ratio may be associated with a targeted reduction in the limestone amount, probably because of the need for raw material transportation at long distances. All the results obtained show lacking specific recipes in the mortar preparation.

Conclusions

Based on the results obtained from X-ray fluorescence, chemical, and powder X-ray diffraction analysis and the discussions on them, the following conclusions are formulated:

- The studied mortars were defined as lime mortars without hydraulic properties prepared without a specific recipe. This mortar type was associated with the application as a permeable binder, protecting against mold at church buildings.
- The phase composition of studied mortars and its comparison with the rocks mineral composition proves the use of only local raw materials, namely sandy limestone (for binder) and gneiss (for aggregate). The results determine the local mortar production and people's good knowledge of the environment during Late Antiquity.

Such results are of fundamental and practical uses allowing future archaeological interpretation and adequate restoration and conservation of archaeological sites.

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